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The Electrolytic Deposition of Brass

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THE ELECTROLYTIC DEPOSITION OF BRASS

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION# BY

Paul Edward Howe,

ENTITLED The Electrolytic Deposition of Brass,

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science,

S. W. Parr

HEAD OF DEPARTMENT OF Chemistry.

- The work of this thesis was done under the immediate direction of Professor A. T. Lincoln.

INTRODUCTION.

Brass was first deposited, from a solution composed of the cyanides of copper and zinc dissolved in a solution of potassium cyanide, in 1841 by H. DeRuolz. Since then brass and other alloys have been deposited and used in technical work; but, little literature has been published except that which appears in the technical handbooks and treatises on electroplating.

Notwithstanding the great practical importance that would result from a successful method of depositing brass electrolytically very little work has been published on this subject. In the literature which does appear considerable confusion arises from the use of the term, current. It is very difficult to determine, when the word current is used, whether current strength or current density is implied. This is not quite so noticeable in the more recent works.

When a solution of two metals is electrolysed the less positive metal has a tendency to separate out first. This attributed to the lower decomposition voltage of that metal. In the case of copper and zinc, the copper,-being less positive than zinc,-has a greater tendency to go out of solution than the zinc. So that if only a weak current be used the less positive metal will separate out first and if the current strength be increased some of the more positive metal will separate out also and the ratio of the two will increase with the current density. This fact has been explained by determining the decomposition voltages

of the various metals. The decomposition voltage of a copper cyanide solution is about 0.61 volts and that of a zinc cyanide solution 1.08 volts. If a current be passed thru a mixture of the solutions, but little zinc will separate out until the pressure is raised to 1.08 volts., but the copper will begin to deposit at 0.61 volts. Hence the proper regulation of the current strength is necessary to produce a deposit of brass of a given composition. A brass high in copper can be obtained by keeping the voltage low while by raising it a brass containing more zinc can be obtained.

The technical handbooks and works on electroplating do not give specific directions as to the method of controlling the percentage composition of brass or other alloys. But Lease[4] drew certain conclusions as to the conditions affecting the deposition of brass. He says,-- "the percentage of copper and zinc cannot be controlled entirely by the current density, it may be controlled closely enough to obtain a good adherent deposit of brass for ordinary work,----it was found that a good looking brass can be deposited electrolytically at current densities as high as 1.2 amperes normal density. The temperature affects the current efficiency more than the nature of the deposited brass,--- the changing conditions in the bath itself affect the percentage of copper and zinc in the deposit much more than the temperature".

Spitzer[5] states that the color of the brass varies with the current density, from a reddish or copper color to a greenish yellow. And also that the zinc content increases with a rising current density only between 0.001 and 0.003 amperes per square

centimeter; and that beyond 0.003 amperes per square centimeter, it does not hold. But Spitzer in his work used such small quantities that full credence cannot be given to his results. In some cases the quantities of brass deposited were so small, amounting to only a few milligrams, that the experimental error was undoubtedly very large.

The object of this thesis is to study the factors entering into and controlling the composition of brass when deposited from a solution of the cyanides of copper and zinc, known as Roseleur's Solution.

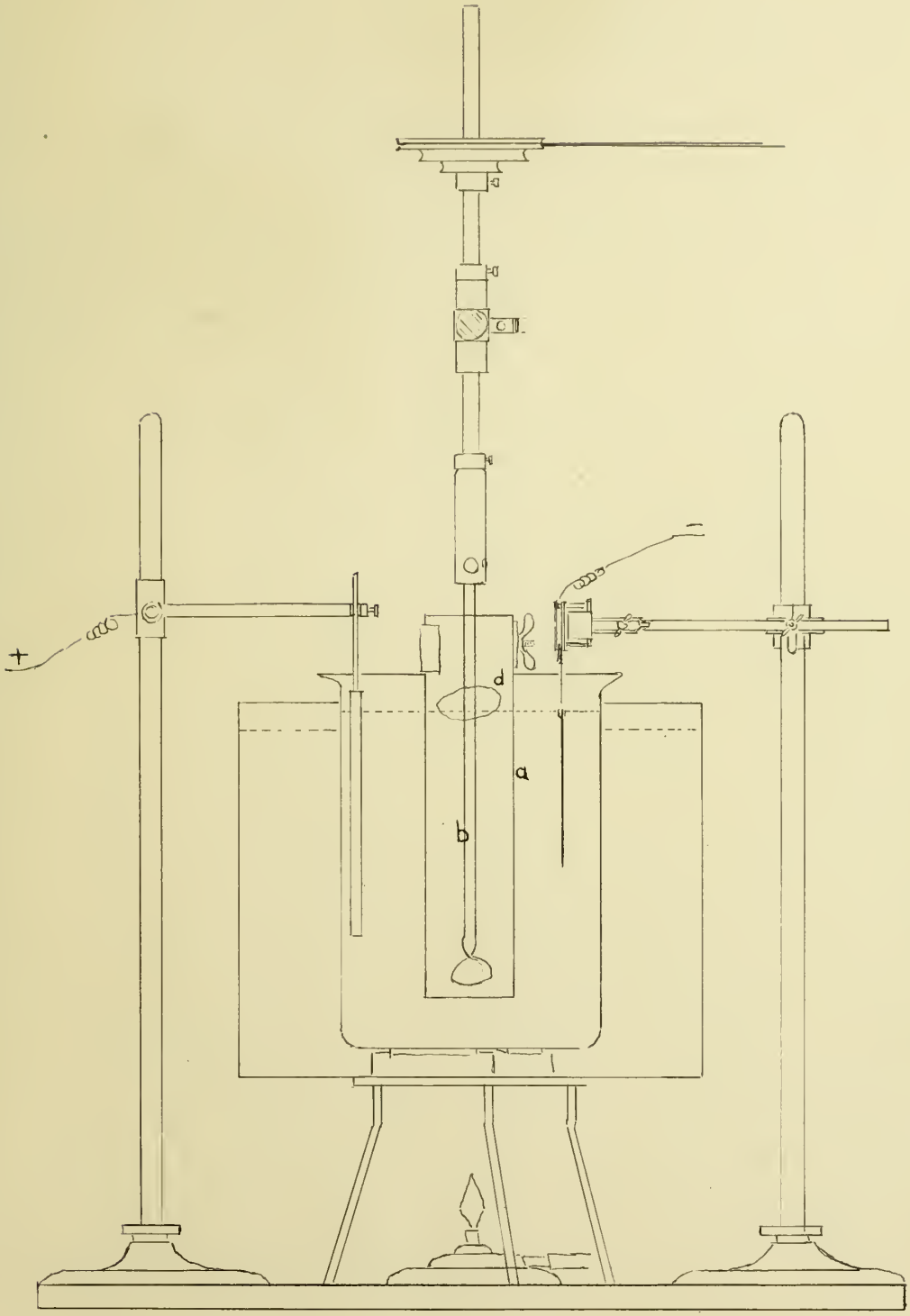
DESCRIPTION OF APPARATUS.

In these experiments Roseleur's Solution was used. This was chosen because it is a solution which was evolved out of the practical experience of technical electroplaters and also because it is comparatively simple, containing but few substances besides the cyanides of copper and zinc.

The Anodes used were of cast brass (74% copper and 26% zinc--1"x1½"x¼"--). Later, to check the results, a larger anode was used which consisted of four strips of brass soldered together, thereby presenting a large anode surface. The cathodes were of three kinds, 1st, sheet platinum (#1-35 sq. cm. and #2-30 sq. cm.) 2nd, platinum gauze (#3-approx. 20 sq. cm.) and, third (rotating) platinum crucibles 22 sq. cm. outside area.

In depositing the brass it was necessary to keep as many

FIGURE-1 BATH



of the factors as possible under control. Hence the depositions were effected at constant temperatures by having the bath immersed in a thermostat. The plating solution was worked in a beaker of about 900 c.c capacity, which was placed in a water bath heated by a micro-chemical burner.

In order to get an even deposit it was necessary to keep the solution thoroughly agitated and yet not set up any positive currents, since this caused streaks or uneven deposits which, under ideal conditions, would not appear. To accomplish this a stirrer was devised which caused a thorough agitation without causing any very marked current in the bath. This device consisted of a glass tube ("a" fig. I) with both ends open, in the side of which was blown a hole (d) at such a height that the level of the bath was just above the lower edge of the hole when the bottom of the tube was about a half inch from the bottom of the beaker. The upper portion of the tube forming a means for holding the tube in the solution. Inside this tube was rotated a glass stirrer (b). With this stirrer a current was set up in a vertical plane; the solution entering either at the top and being forced out at the bottom or at the bottom and being forced out at the top, depending upon the direction of rotation. At one side was hung a glass plate which extended to the bottom of the stirring tube, in this manner effectively stopping any currents which might be set up in a horizontal plane. The thermostat was agitated by a propeller shaped glass stirrer.

The anode was suspended in the solution by an insulated stand. The cathodes were suspended by a platinum wire from a

FIGURE-2 CATHODE SUPPORT.

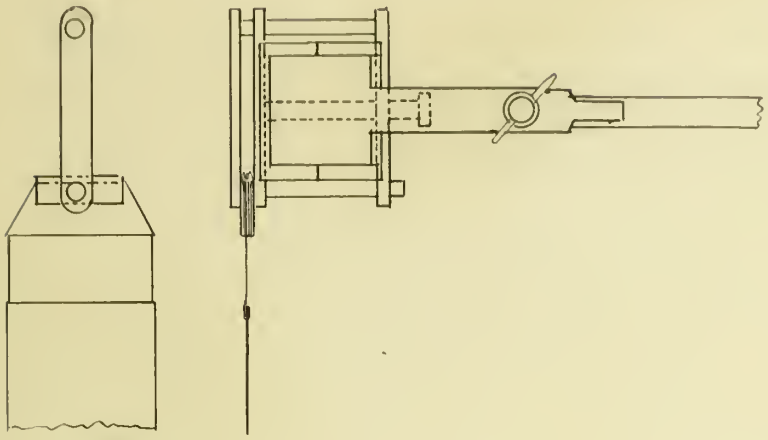
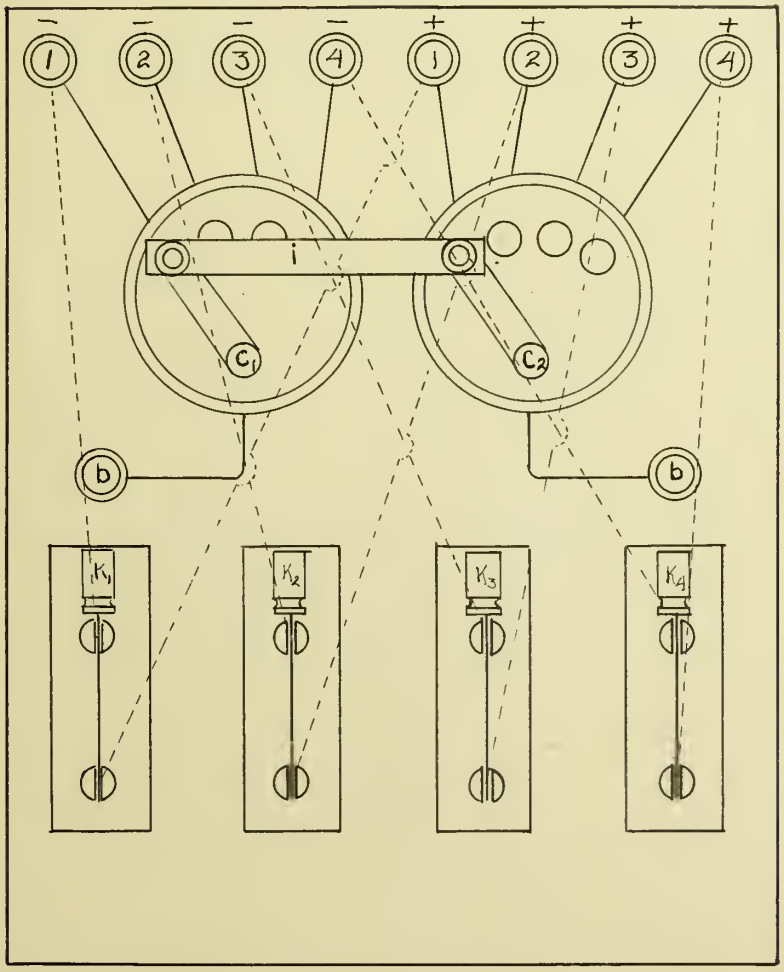


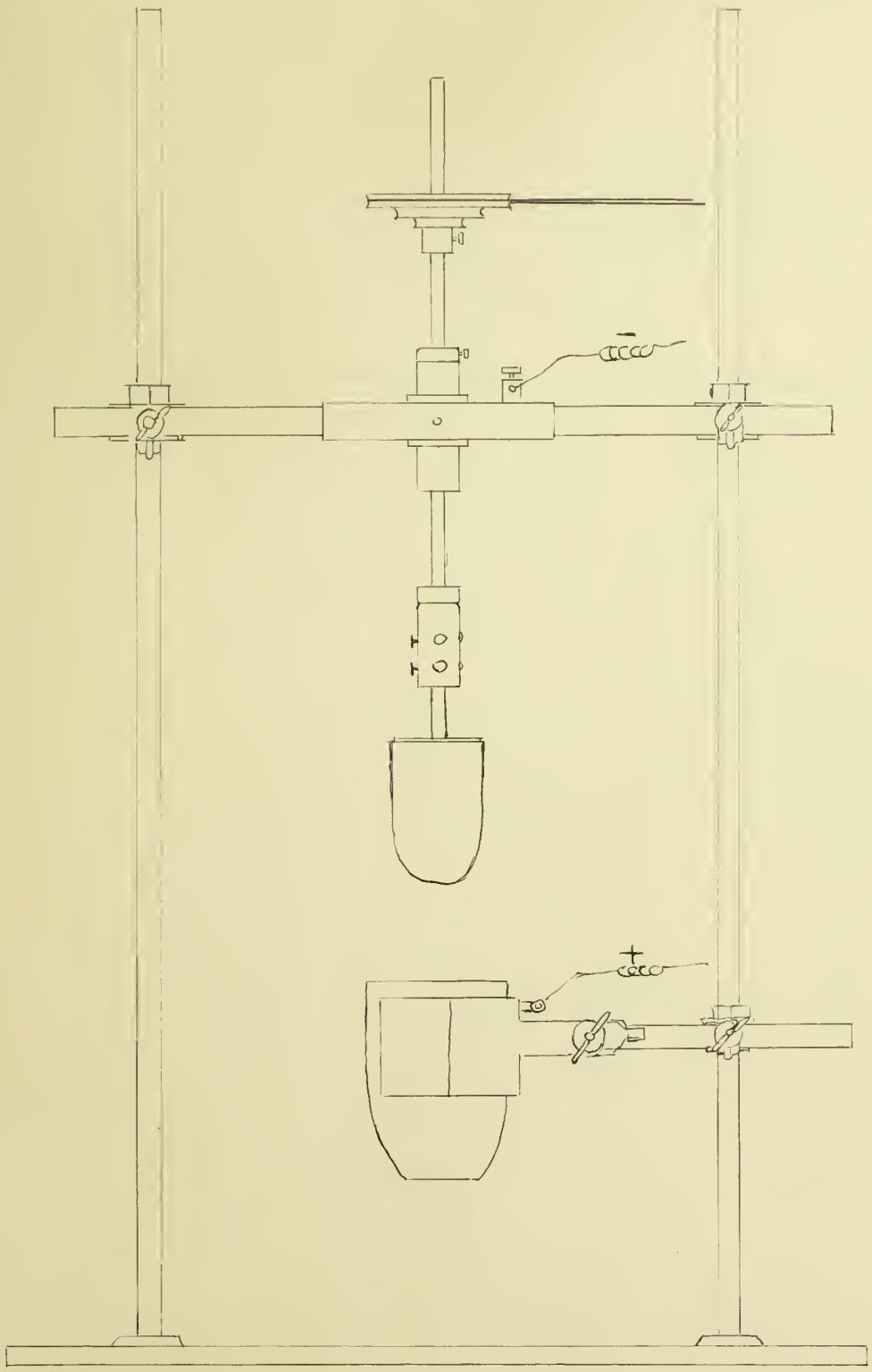
FIGURE-3 SWITCH BOARD



piece of wood cut in the shape of a trapezoid, grooved on the edges and covered with a piece of sheet copper bent so as to form a groove in which the loop of the cathode fitted (Figure 2). This device, with the cathode in place, was held in a brass clamp to which the wire from the battery was fastened.

The voltmeter was attached at the terminals of the two electrodes, the circuit being made with a switch. The ammeter was connected in the circuit by means of a switch which permitted the use of the ammeter for four different experiments without disconnecting the instrument. The switch board (Figure 3) consisted of eight terminals or binding posts, the first four being negative and the second four positive, to which the leads from the various experiments could be attached. Two other terminals (b-b) were connected with the central poles of the two, four-point, circular switches; one negative and the other positive, and to these the leads from the ammeter were attached. To the four points on the circular switches were run wires leading to the terminals (1,2,3 etc.). Those from (c_1) being attached to the negative terminals and those from (c_2) to the positive terminals. The contacts on the two switches were connected by a piece of rubber (i), thus insulating them from each other and enabling the two contacts to be moved at once, preventing any accident due to the connection of two different circuits which would happen should the switches be thrown separately. Below the circular switches were four knife switches (k), the upper ends being connected to the negative terminals and the lower end to the positive. So that in order to take a reading with the ammeter, the switch (c)

FIGURE-4 ANALYSIS



was thrown to the contacts corresponding to the desired experiment and the corresponding knife switch opened, which would throw in the ammeter.

The analysis of the resulting brass was effected by means of the rotating cathode, (figure 4). A platinum crucible having a rounded bottom was fastened to a rotator by means of a rubber stopper. The stopper being connected to the rotator with a brass rod inserted into the hole in the center of the stopper. To the lower end of the rod a copper brush of fine wire was soldered, thus making a contact with the crucible. The other end of the rod was held by the rotator, thereby making the electrical connection. The anode was a crucible of larger dimensions (60 c.c.) held by a condenser clamp. The electrical connections being made with a piece of brass which lined one side of the clamp. The two leads (one from the rotator and the other from the large crucible) were connected to the ammeter board so that the current used could be determined and also to determine when the washing was complete. The electrolyte was siphoned out with a small glass tube, which was connected with a rubber tube to the drain. Water being poured in at the same time that the electrolyte was siphoned out until the ammeter read zero, then the current was shut off and the cathode dried and weighed.

DISCUSSION OF DATA AND RESULTS.

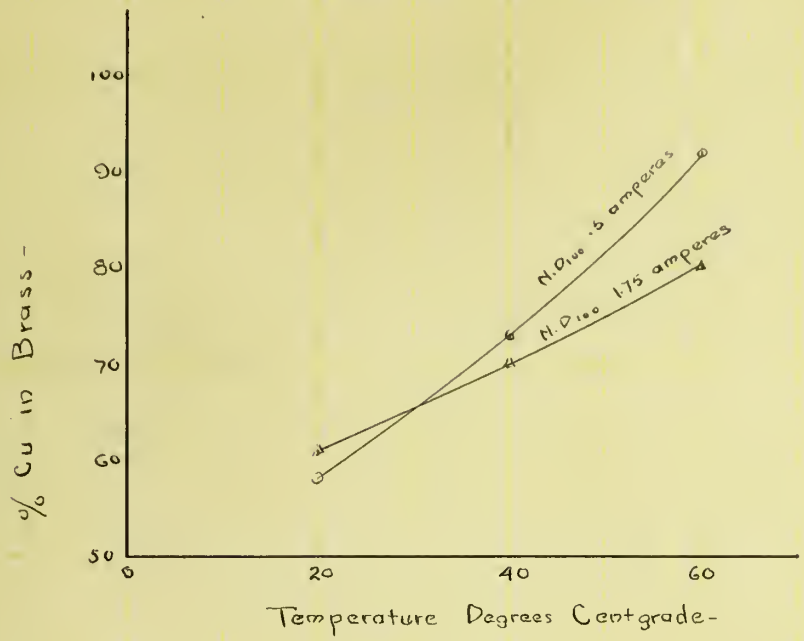
(a) The Effect of Temperature on the Percentage Composition of Brass; is shown by a series of experiments run at different current densities for two temperatures (20°and 60°C.)

TABLE-I

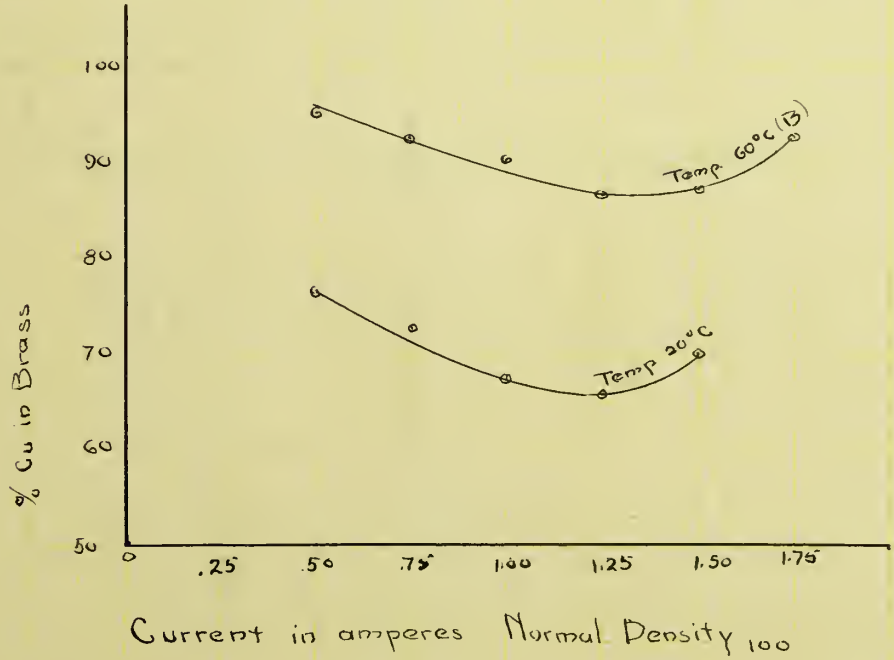
Normal Density Amperes/Sq.cm.	Percent of Cu at 20°	Percent of Cu at 40°	Percent of Cu. at 60°
.50	60.	68	91.6
.50	58	73	91.7
1.75	62	69.5	79.8
1.75	59	70.8	80.5

As can be seen from table #1 and by curve #1, for the same normal density with an increase in the temperature there is an increase in the percent of copper in the deposited alloy.[4] These results are represented in Table 1. The first column represents the normal density or amperes per square decimeter, investigated, the second column the percent of copper deposited at 20° C. for the various current densities, the third column the percent of copper at 40°C. and the fourth column that at 60° C. This variation is probably due to a decrease in the resistance of the bath accompanying the rise in temperature (see curve #3 showing the relation between the resistance of the solution and the increase in temperature.) That is, since the current density is constant, an increase in the temperature causes a decrease in

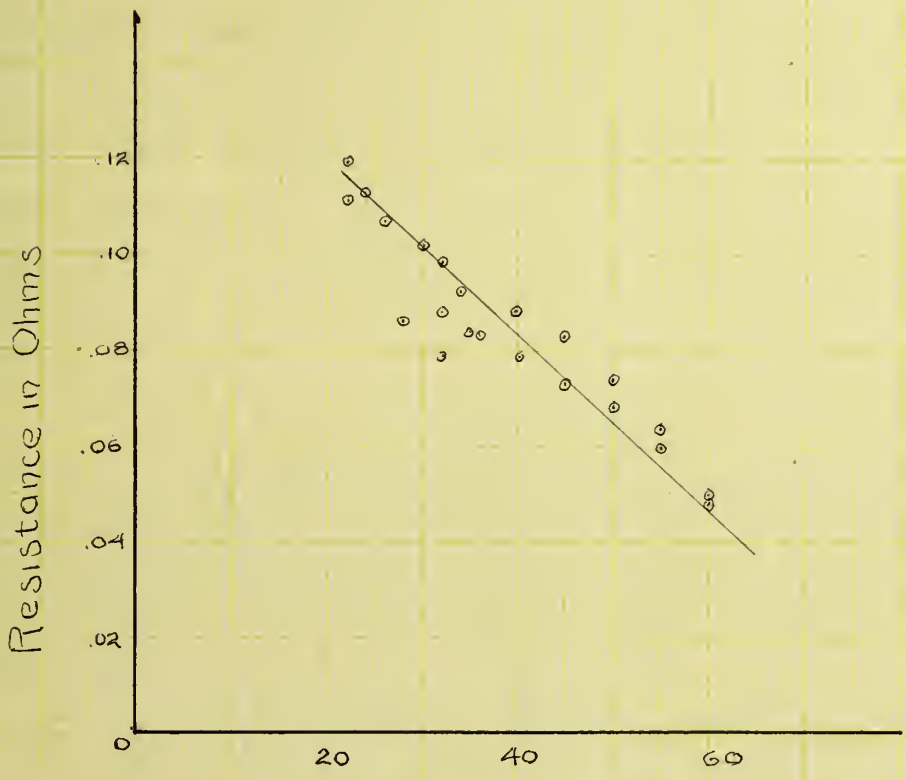
Curve * 1 - Showing Relation Between the % of Cu in Brass and the Temperature for .50 and 1.75 Amperes Current $N.D_{100}$.



Curve * 2 - Showing Relation Between % Cu in Brass and the Current $N.D_{100}$ For 20 and 60 Degrees Centgrade.



CURVE *3 SHOWING RELATION BETWEEN THE RISE IN TEMPERATURE AND THE RESISTANCE OF ROSELEUR'S SOLUTION.



resistance hence the voltage is lower and approaches the decomposition voltage of the zinc, so that less zinc and more copper is deposited.

(b) The Effect of Change in the Cathode Current Density on the Percent of Copper in Brass: is shown by a series of experiments run at varying current densities for two temperatures. From Table #2 and curve #2 it is seen that within the range of current densities studied with an increase in the current density there is a decrease in the percent of copper in the alloy, up to a certain limit where the percent of copper begins to rise. This limit was reached at a lower normal density at 20°C than at 60°C. In table #2 are the results of three series of experiments. The

TABLE-II

Temperature	% Cu - $N.D._{100}$ .50 Amperes	% Cu - $N.D._{100}$ .75 Amperes	% Cu - $N.D._{100}$ 1.00 Amperes	% Cu - $N.D._{100}$ 1.25 Amperes	% Cu - $N.D._{100}$ 1.50 Amperes	% Cu - $N.D._{100}$ 1.75 Amperes
20° ×	76.3	73.0	67.5	65.6	70	....
A 60° ⊙	92.7	---	85.6	....	....	79.8
B. 60°	95.0	92.5	90.5	86.4	87	92.6

× Average of two results

⊙ Average of three results.

first (A) series at 60°C. was made at but three normal densities hence the bend in the curve is not present. But in the second (B) series at 60°C, which was made with a larger anode of a different composition, the bend is present which leads us to our former

conclusion. Spitzer's[5] results show this but he does not seem to have made any note of it or noticed the variation.

In the deposition of brass the voltage for a given cathode current density is dependent upon the condition of the anode. In all experiments the anode was clean at the beginning of a deposition. But at the end of some runs the anode would be coated with a green slime or scum, (R-2-1) and the external resistance would have to be varied to keep the current density constant, the voltage rising at the same time. This would take place until the pressure was approximately 3 volts and then remain constant. The pressure always started at about 1.8 to 2 volts and rose to approximately three volts in from two to eight minutes, except that in rare cases it took a greater time. This variation in pressure was most noticeable at 20°and 40°C. At 60°C it did not occur as frequently as at the lower temperatures. In a later series a large anode surface was used (10 times the area of the cathode). With this the current density was kept more nearly constant, the pressure rising only when the anode became coated with a black slime, which would disappear upon the addition of a few milligrams of K C N.

(c) The Effect of the Concentration of the Bath on the Percent of Copper in the Brass. During the preliminary experiments the percent of copper in the brass began to grow less when it should have increased. The experiments were continued, analysis of the bath being made (the weight of copper in 10c.c. of a new bath being taken as unity.) which showed that as the bath was continued in use the copper per 10 c.c. of the solution decreased

and this was accompanied by a decrease in the percent of copper in the brass. This series which covered a range of three temperatures, showed quite conclusively that the percentage composition of the deposited alloy was dependent upon the condition or concentration of the bath.

This depletion of the bath is explained by the fact that the copper being less electro-positive than the zinc tends to go out of solution and deposits more readily and at a lower pressure than the zinc, so that the bath becomes low in its copper content, causing variations in the composition of the deposited alloy.

(d) The Ratio of the Anode-loss to the Cathode-gain. In the preliminary experiments the ratio of the anode-loss to the cathode-gain was determined. The anode being weighed before and after each deposition. The ratio approached unity, but varied so much that it did not seem to carry any great weight.

This variation was no doubt due to the fact that the anode became coated with a green slime, which, when cleaned off introduced an error. For, this accumulation of green slime did not represent an equal replenishment of the bath for a given amount of brass deposited out of solution. The ratio would be of great importance as long as the anode could be kept clean during each operation.

(e) The Character of the Brass Deposited. The color of the brass varied from a reddish yellow or nearly copper color down thru the various shades to a yellow brass. The color varied with the percent of copper contained in it. The red brass being high in copper (85-95%) and the yellow brasses were low (60-70%).

The deposits were, in most cases, good even, adherent deposits being obtained at a normal density of 2.0 amperes per square decimeter during runs of one to one and a half hours. The deposits, in the case of the stationary sheet platinum cathodes, had a dull color as distinguished from the brasses obtained with the rotating cathode, which were bright and had a polished appearance. Except that at the high current densities and after long runs the surface would be dull. Any positive currents set up in the bath produced nodules on the edges, of the sheet platinum, from which the current first struck the cathode. But under ideal conditions this would not happen.

In the case of the rotating cathode, nodules or heavier deposits would form on the end of the crucible. The roughened places appearing as streaks which radiate from the bottom of the crucible up onto the sides, following the path of a spiral. Also any uneven surface on the crucible filled up with a rough deposit, for this reason it is necessary in using a rotating cathode to have a perfectly smooth surface.

The platinum gauze showed fewer of the effects of currents in the solution and took a good deposit. But it was not used during the determination of the effect of the current density because its area could only be determined approximately, and hence the results could not be compared with the determinations made on sheet platinum in the same series.

(f) In the Analysis of the Deposited Alloys, the weight of the platinum crucible being known, by a second weighing the

amount of brass was obtained; this brass was dissolved up in concentrated nitric acid and the volume made up to 50 c.c. Of this solution 10 c.c. were taken out with a pipette-, the same pipette being used in all analyses, and the copper was determined electrolytically, the zinc being obtained by difference. In this manner good adherent deposits of copper were obtained free from zinc.

SUMMARY.

From a consideration of the experimental data herein presented we have shown that:-

(1) The temperature affects the percentage composition of the electrolytically deposited alloy. An increase in the temperature increasing the percent of the metal having the lower decomposition pressure.

(2) The Normal Density affects the percentage composition. An increase in the normal density giving a decrease in the percentage composition of the less positive metal, up to a certain normal density (depending upon the temperature) and then an increase in the percentage composition.

(3) The composition of the alloy is affected by changes in the concentration of the bath. The percent of the less positive metal decreasing as the bath becomes depleted.

(4) In addition we have devised.

(a) A convenient method for taking ammeter readings from a number of different sources with the same ammeter.

(b) A method of stirring a bath so as to give a thorough agitation of the solution without setting up any positive currents.

(c) A method for the electrolytic analysis of substances using small quantities of the liquid to be analysed and affecting a complete deposition of the metal sought (copper) in quantities of .02 grams in an hour or less.

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